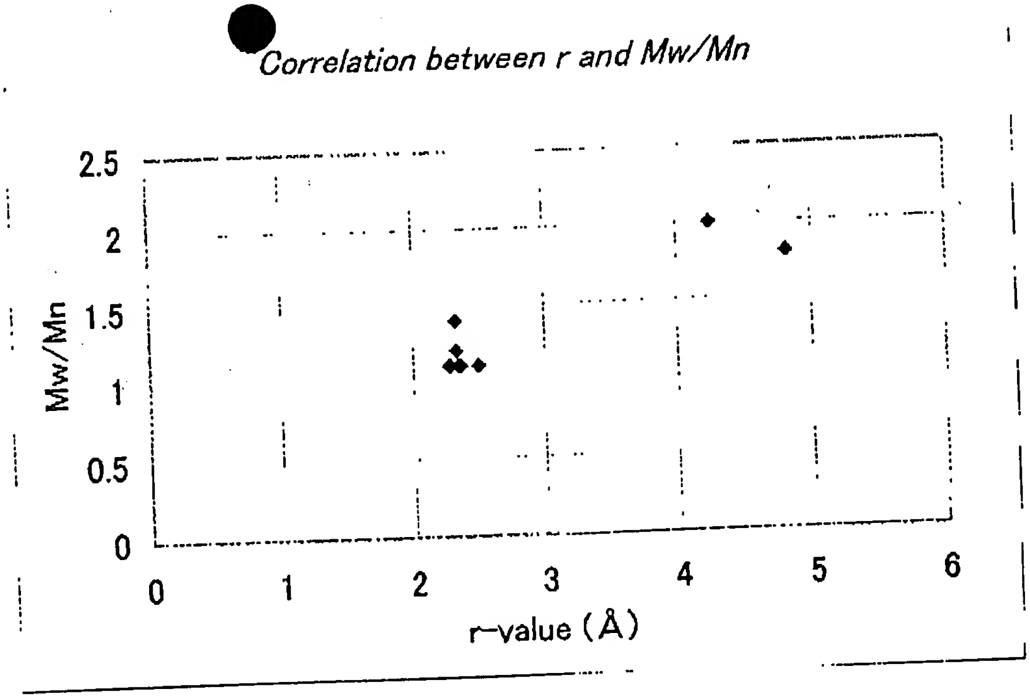
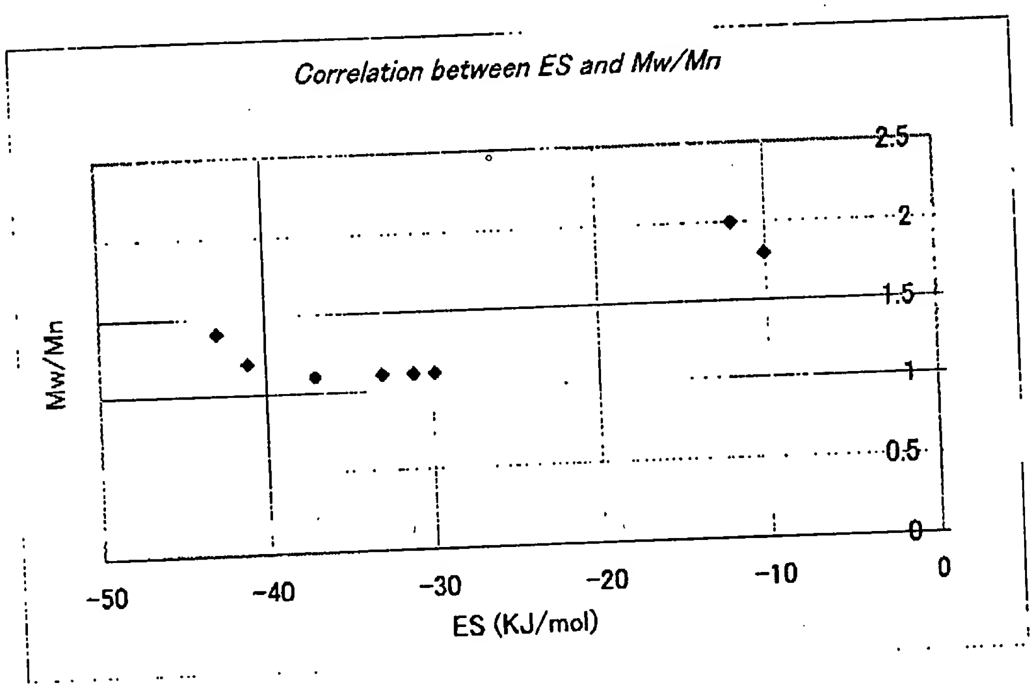

Correlation between r and Mw/Mn
Mw/Mn
2.5
2
1.5
1
0.5
0
0
1
2
3
4
5
6
r-value (Å)


Correlation between ES and Mw/Mn
Mw/Mn
2.5
2
1.5
1
0.5
0
-50
-40
-30
-20
-10
0
ES (KJ/mol)

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INDUSTRIAL ORGANIC CHEMICALS

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To
Anthony Jacob, Bessie, David, Debbie,
Michelle, Ralph, Ted, and Virginia.

density and linear low-density polyethylene (LDPE and LLDPE). These are the three important forms of polyethylene. Growth in the 1990s is projected at about 2% higher than that of the gross domestic product.

3.1.1 Discovery of Low- and High-Density Polyethylenes

The discovery of LDPE in 1932 was serendipitous. Fawcett and Gibson at ICI in England were actually studying chemical reactions at high pressures with a view to making synthetic rubber from ethylene and benzaldehyde. The discovery hinged on a leaking autoclave. It had been pumped up to reaction pressure and allowed to stand over the weekend prior to the carrying out of the reaction. Pressure had been lost because of a leak, and more ethylene was added to the reactor which, at this stage, contained traces of oxygen. To the surprise of the chemists, the pressure refused to rise. The reactor turned out to be full of a white powder and the benzaldehyde was intact. After many more experiments, it was realized that oxygen was serving as the initiator.

The conventional wisdom of the 1930s dictated that polyethylene could not be made, because it was not possible to put sufficient energy into the ethylene molecule to achieve the transition state. This is, however, quite possible with pressures in the range of 2000 bar and a temperature of 200°C in the presence of a free radical initiator such as oxygen or various peroxides. The polymerization is carried out in the gas phase, high pressures favoring the propagation reaction, which is in part a function of ethylene concentration. Termination, on the other hand, is independent of ethylene concentration.

The discovery of HDPE was similarly serendipitous by investigators at Standard Oil of Indiana and Phillips Petroleum seeking to oligomerize ethylene to gasoline-size molecules. Whereas LDPE finds its greatest use in the manufacture of film, the stiffer linear high-density material has its major uses in the manufacture of bottles by blow molding and in structural parts by injection molding.

The first linear polyethylene was probably made in 1950 at Standard Oil of Indiana by Zletz, where it was observed that a molybdenum oxide catalyst on silica at mild temperatures and pressures did not give oligomers, but rather high-density polyethylene. Soon thereafter, Banks at Phillips Petroleum obtained similar results with a catalyst comprising chromium oxide supported on silica or alumina. Phillips developed and licensed its process aggressively.

In 1954 Ziegler announced his discovery. He was successfully studying ethylene oligomerization reactions (Section 3.3.2) based on aluminum alkyls. A metal salt impurity in the reaction mixture led to the formation of high molecular weight linear polyethylene. From this evolved the famous Ziegler catalyst, typical of which is a combination of aluminum triethyl with titanium tetrachloride. The Ziegler process attracted great theoretical as well as practical interest, because it can be applied to propylene and to practically any unsaturated compound, unlike the metal oxide processes, which are effective, for practical purposes, only with ethylene. Chromium-based catalysts dominate the

production of polyethylene in the United States, although the Ziegler process is used to the extent of 60% in Western Europe. The latest development is the use of metallocenes or single site catalysts. These are described in Section 15.3.12.

3.1.2 Low-Density Polyethylene

Low-density polyethylene may be manufactured batchwise in an autoclave or, more commonly, in a tubular reactor that makes possible continuous processing. Batch-produced product is useful for paper coating, where its highly branched structure is advantageous. The somewhat less branched continuously produced product is useful for film. About 35% of the ethylene is allowed to react in the continuous process, and the remaining 65% is recycled. This is termed 35% conversion per pass and is necessary to eliminate excess branching. With HDPE branching is not a problem and conversion may be 100%. The properties of LDPE and HDPE are listed in Table 3.1.

The branched structure of LDPE profoundly affects its properties. Because the polymer molecules cannot get as close together as they can in HDPE, the crystallinity is of the order of 55% as compared to 85–95% for HDPE. The crystalline melting point, softening point, and tensile strength of LDPE are all a function of the branched structure and are considerably lower than the corresponding values for HDPE. On the other hand, the softer LDPE shows higher elongation at break and higher impact strength than does the rigid

TABLE 3.1 Properties of Polyethylenes

	LDPE	HDPE	LLDPE
Initiator or catalyst catalyst—	Oxygen or organic peroxide	Ziegler or Phillips catalyst	Ziegler or Phillips catalyst
Reaction temperature	200–300°C	As low as 60°C	As low as 60°C
Pressure (bar)	1300–2600	1–300	1–300
Structure	Branched	Linear	Linear with short branches
Approximately crystallinity	55%	85–95%	55%
Comonomer	None	None	1-Butene, 1-hexene, or 1-octene
Tensile strength (psi)	1200–2000	3000–5500	2000–2500
Tensile strength (tonnes m^{-2})	850–1400	2100–3900	1400–1800
Elongation at break (%)	500	10–1000	500
Density (g cm^{-3})	0.915–0.925	0.945–0.965	0.915–0.925

HDPE. It is also translucent rather than opaque because of its lower crystallinity. The difference in densities, which characterizes the two polymers, is of the order of 0.3–0.4 g/cm³. The density of LDPE may be as low as 0.915 g/cm³ and of HDPE as high as 0.965 g/cm³.

3.1.3 High-Density Polyethylene

Most HDPE is actually a copolymer containing up to 4% of 1-butene or less commonly 1-hexene. The comonomer is required, particularly when metal oxide catalysts are used, to avoid formation of molecular weights so high that the polymer becomes intractable. The copolymer also has improved low-temperature properties.

The production of HDPE is much less energy intensive than that of LDPE. Reaction temperatures can be as low as 60°C and pressures as low as 1 bar. Nonetheless, temperatures of 130–270°C and pressures of 10–160 bar are used commercially. Conversion per pass approaches 100%.

High-density polyethylene is manufactured in solution, slurry, or fluidized bed processes. In the slurry process, the catalyst is dispersed in a solvent such as hexane, and the ethylene is polymerized batchwise in a series of reactors. The gas phase, fluidized bed process was devised by Union Carbide, BP, and others. Small HDPE particles are fluidized by gaseous ethylene and comonomer (e.g., 1-butene) at 85–105°C and 20 bar. Catalyst is continuously sprayed into the reactor. The ethylene and comonomer copolymerize around the preformed polymer particles. At the same time, the gaseous ethylene removes the heat of reaction.

The initial particles grow to an average diameter of 500 μ over a period of 3–5 h, during which time only about 2–3% of the ethylene polymerizes. The unconverted reactants are recycled. Polyethylene, once prepared, is melted, mixed with stabilizers and other additives, and extruded to form spaghetti-like rods, which are then cut into small pellets. The extrusion is an energy-intensive operation. An objective of the fluidized bed process, not achieved initially, was to obtain the polymer as a powder that could be used as such for molding and extrusion. Further development has apparently made this possible, although the value of the powder is questionable, because its low-bulk density increases shipping costs. Even so, the gas-phase process has proved to be an economical way to prepare both HDPE and LLDPE and has been licensed extensively.

3.1.4 Linear Low-Density Polyethylene

Linear low-density polyethylene is the successful result of a desire to prepare LDPE by the less energy-intensive conditions used for HDPE. High-density polyethylene copolymers with high comonomer content have been known for many years. Their density was less than that of HDPE, their crystallinity was lower, and the properties that depended on crystallinity were altered. Considerable time elapsed before it was recognized that a copolymer of HDPE, in which

crystallinity had been reduced to about 55% (the crystallinity of LDPE, see Table 3.1) and its density to about 0.925 g/cm³ had many of the characteristics of LDPE. Thus a copolymer of ethylene and 6–8% 1-butene resembles LDPE. Like the other polyethylenes, it may be manufactured by solution, slurry, or fluidized bed processes.

The fact that products of this type were known before they were recognized as economically advantageous replacements for LDPE emphasizes the importance not only of discovery but of its recognition.

Linear low-density polyethylene, like LDPE, has branching that inhibits close approach of polymer molecules and decreases crystallinity. The branching in LDPE is irregular and, if the LDPE is prepared by the autoclave process, there are secondary branches on the primary ones. LLDPE has regular branching because of the pendant C_2 groups provided by the 1-butene comonomer. This uniformity makes possible closer association of the polymer molecules in the crystalline portion, for which reason LLDPE has a higher tensile strength than LDPE, allowing the use of thinner or lower gauge films.

Its growth in the United States was rapid at first and almost completely at the expense of LDPE. Growth was facilitated because LLDPE could be processed in HDPE equipment. Subsequently, new uses for it were found in stretch wrap film, injection molding, and rotomolding—applications for which LDPE is not suitable. The cost advantage provided for LLDPE manufacture by lower energy use is in large part counterbalanced by the cost of the more expensive monomer, 1-butene, which became one of the fastest growing chemicals of the mid 1980s. Newer processes for LLDPE make use of 1-hexene, 1-octene, and 4-methyl-1-pentene as comonomers.

1-Butene for LLDPE may be obtained either by dimerization (Section 3.3.1) or oligomerization (Sections 3.3.2 and 3.3.3) of ethylene or by isolation from the C_4 olefin stream from steam or catalytic cracking (Chapter 5). In fact, practically all of it in the United States and Western Europe is obtained from the last source, which underscores the point that refinery processes usually are more economical than processes in chemical plants. Saudi Arabia makes 1-butene by dimerization of ethylene (Section 3.3.1) since refinery 1-butene is not available. 1-Hexene and 1-octene are obtained solely by ethylene oligomerization and 4-methyl-1-pentene by propylene dimerization (Section 4.2).

3.1.5 Very High Molecular Weight Polyethylene

Very high molecular weight polyethylene with a density of 0.941 g/cm³ or higher is not used widely because it is difficult to process. It is made under HDPE conditions without comonomer and is used primarily for plastic ropes. One of its interesting newer applications is for the preparation of high-strength polyethylene fibers. Tensile strength in polymeric fibers may be increased by drawing, a process that causes the polymer molecules to crystallize or to align themselves so closely that physical forces of attraction between polymer molecules come into play. However, physical stretching does not cause uncoiling of